

First-Principles Modeling of the Stability of Layered Li-Battery Electrodes

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Overview

Computer simulation has been applied to model various aspects of lithium batteries, including, at the macroscopic level, the kinetics of Li currents in the electrodes and electrolytes and the effect of the solid-electrolyte interface, and at the microscopic level, the electronic structure and atomic dynamics of battery components at the nano scale. We are exploring, both experimentally and with simulation, microscopic features such as the structural chemistry and phase stability of candidate electrode materials and their effect on macroscopic measures of battery performance. This poster presents (microscopic) quantum mechanical simulations related to phase stability in a prominent class of battery cathodes.

Introduction

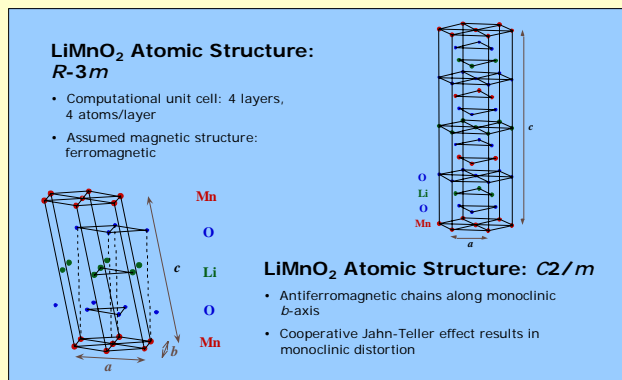
- Electrode phase stability and structural integrity during Li insertion/extraction cycling critical to the performance of Li batteries
- Simulation with first-principles *density functional theory* methods enables phase stability predictions both for pristine electrode materials and in the presence of dopants introduced to enhance performance

Layered LiMn/MO₂ Electrodes

- Advantages include high capacity, low Mn cost, and low toxicity
- Disadvantages include Jahn-Teller activity of Mn³⁺, transformation to spinel upon Li extraction, and decomposition upon overdischarge
- Dopants often introduced to remedy disadvantages

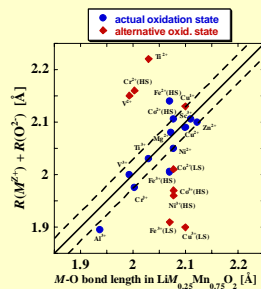
Dopant-Induced Stabilization of *R*-3*m* Structure against Jahn-Teller Distortion to *C*2/*m* Structure

- Simulations performed to assess relative stabilizing properties of series of dopants at concentration $x=0.25$
- Local-spin-density-approximation with generalized gradient approximation correction (LSDA-GGA) applied, as implemented in VASP code



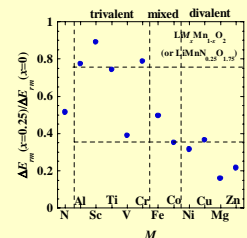
Oxidation States in *R*-3*m* Structure

- Plot compares calculated M-O bond lengths in LiMn_{0.25}Mn_{0.75}O₂ with those based on standard ionic radii
- Oxidation states 3+ (2+) for M earlier (later) than Fe, Co
- Fe, Co less oxidized in *R*-3*m* than in *C*2/*m* structure (not shown)



Stabilization of *R*-3*m* Structure by Row-3 Element Dopants

- Energy difference between rhombo and mono structures at composition LiMn_{0.25}Mn_{0.75}O₂
- Smaller values mean greater stabilization
- Divalent dopants, with filled subshells (e.g., Ni, Mg, Zn), are most stabilizing

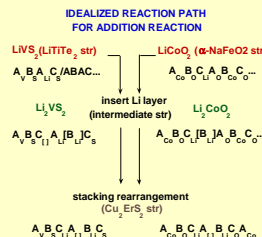


Overdischarge: Adding Li to *R*-3*m* LiMO₂ (*M*: Mn, Co, Ni)

- Three reactions possible:
Li + LiMO₂ = Li₂MO₂ (addition)
Li + LiMO₂ = MO + Li₂O (decomposition)
3Li + LiMO₂ = 2Li₂O + M (extrusion)
- Addition reaction desirable, because it enhances capacity and overall reversibility of insertion/extraction cycling

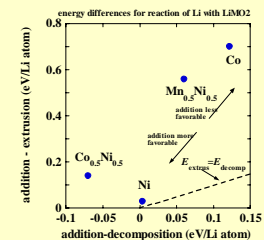
Relationship between the Different Overdischarge Reactions

- One expects that, for most *M*, addition reaction will be favored *kinetically* (idealized reaction path shown below) whereas decomposition and extrusion reactions will be favored *thermodynamically*
- We hypothesize that addition reaction will occur in those systems for which the thermodynamics is not too unfavorable



Reaction Energy Simulations (GGA+U Method)

- Extrusion always the most favored reaction thermodynamically
- Upper right (lower left) region of plot less (more) favorable for addition reaction: M=Co undergoes no addition reaction, but M=Ni and Mn_{0.5}Ni_{0.5} do
- Co_{0.5}Ni_{0.5} appears a good candidate for addition reaction



Conclusions

- Divalent dopants *M* stabilize LiMn_{0.25}Mn_{0.75}O₂ against Jahn-Teller distortion (for different reasons, divalent dopants also stabilize against transformation to spinel [Reed and Ceder 2004])
- Based on calculated reaction energies, LiCo_{0.5}Ni_{0.5}O₂ appears a good candidate for undergoing an addition reaction upon overdischarge

Concluding Perspective

Our quantum mechanical calculations have provided a fundamental understanding of the behavior of a series of dopants that are commonly employed in battery cathode materials. Although the results were obtained for layered structures, similar behavior is also expected for spinel, another prominent class of electrode structures of interest for lithium battery applications.